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(54) **Title:** BIOBASED COATING FOR IRON COMPRISING SURFACES

(57) **Abstract:** The present invention is in the field of a composition for forming a bio-compatible membrane applicable to building material, such as steel, stainless steel, iron alloy, cast steel, etc., to a method of applying said composition for forming a bio-compatible membrane, a biocompatible membrane, use of said membrane for various purposes, and to building material comprising said membrane.



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Biobased coating for iron comprising surfaces

FIELD OF THE INVENTION

The present invention is in the field of a composition for forming a bio-compatible membrane applicable to building material, such as steel, stainless steel, iron alloy, cast steel, etc., to a method of applying said composition for forming a bio-compatible membrane, a biocompatible membrane, use of said membrane for various purposes, and to building material comprising said membrane.

BACKGROUND OF THE INVENTION

Steel is an alloy of iron and a small amount (0.002 wt. % and 2 wt.%) of carbon. There may be additional elements present in steel, such as manganese and phosphorus. In order to adapt properties of steel typically additional metal alloying elements are added.

Steel is produced in huge quantities every year. Iron and steel are used widely for construction purposes, e.g. for shipbuilding, for pipelines, in mining, in infrastructure and buildings, in vehicles such as cars, in construction materials, and for offshore construction. Many of the application of steel and iron are in an environment that is (relatively) harsh, such as in salty water. As a consequence surfaces of steel and iron being exposed to these harsh environment degrade over time. Such degradation may be limited by applying a coating, such as paint, by adapting properties of steel and iron, etc. These measures are typically costly, rely on environmentally unfriendly materials, such as heavy metals, solvents, polymers, etc. Also coatings need to be applied over and over again, as the coatings themselves degrade as well. For some applications, such as ships and offshore equipment, coatings can not be applied at a site of use; therefore these applications need to be moved, often over a long distance, to (re-)apply a coating.

Applying a coating onto e.g. steel is known.

For instance, US 3,728,267 A recites application of an acidic pickling composition, comprising an at reduced pH film-forming component consisting essentially of sodium alginate or sodium alginate and gelatin, with at least one of

starch, bentonite, talc, powdered silica, and powdered active terra alba, a liquid acid or solid acid, a penetrant and a solution promoting agent. The disclosure relates to a ready removable peeling composition for use in a pickling treatment, which does not call for subsequent treatment, in order to reduce costs. Inherently a peelable film does not adhere well, and hence does not provide much protection.

Further, US 4,851,149 A recites an acid cleaning/pickling composition for metal surfaces containing as essential components (A) at least one protein-derived polymer, sugar-derived polymer, sorbitol, tannin, or vinyl-based polymer, (B) at least one iodine or iodine-affording compound; acids solutions prepared therefrom; and methods for their use. For liquid compositions further essential ingredients are present. Corrosion of the acid in the composition is said to be inhibited, the acid being used to remove deposits, such as scale, from a to be cleaned surface. Hence no coating seems to be formed and the function of the polymer is unclear, apart from being non-toxic.

EP 1 992 595 A1 recite a method for producing a cement-containing material, in particular a cement-containing material having a low content of soluble Cr (VI) which comprises the step of providing a cement-containing material with metallic sulphate particles coated with at least one product of the hydrolysis of a collagen material such as gelatin. The cement (surface) does not provide Fe-cations, nor does a coating seem to be formed, other than presence of a coating on metallic sulphate particles.

US 3,106,496 A recites a process for coating and annealing grain oriented silicon steels. The coating of this document is not water dissolvable. The applied temperature is 700 °C, the goal is to improve the grain structure of the steel, and the coating should provide good separation after application.

FR 1,319,873 A relates to a similar process as the US'496, albeit at an even higher application temperature of 900 °C -1200 °C.

Thus there is a need for improved coatings or membranes which can be applied easily and which provide a good, durable and not readily removable coating or membrane.

The present invention relates to a composition for forming such a membrane, use thereof, and material comprising said membrane, which overcomes one or more of the above disadvantages, without jeopardizing functionality and advantages.

5 SUMMARY OF THE INVENTION

The present invention relates in a first aspect to a method of forming a bio-compatible membrane which can be applied easily and which provides a good, durable and not readily removable coating or membrane, according to claim 1, a
10 method of protecting a surface from degradation according to claim 10, a coating according to claim 11 or 12, a material comprising said coating according to claim 14, and use of the present composition and/or present polymer coating according to claim 15.

15 The invention makes use of non-toxic and environmentally friendly components. These components are biocompatible, i.e. an impact on the biological environment is considered minimal. The composition has as a main liquid water, or may be formed primarily from water. Including a solvent the composition
20 comprises a polymer, and optionally a silicate and a nanoparticle, which form > 95 wt.% of the composition. If no further additives are present these components form > 99 wt.% and typically 99.9 et.% of the composition; in other words apart from unintentional impurities nothing else is present,
25 with the restriction that if naturally base polymers are used, such a microbial alginate, inherently more impurities could be present.

The polymer used is preferably bio-degradable, that is can be degraded by e.g. bacteria, yet is stable enough to
30 provide e.g. a good protection for an underlying material, such as steel. The polymer dissolves sufficiently in water, typically forming a viscous solution. As such ionic polymers, such as in alkaline form, and acidic polymers are considered specifically. The polymer is capable of forming a gel, once
35 being in contact with polyvalent cations, thereby forming a flexible, impermeable membrane. The membrane preserves water being present in an underlying material and protects the underlying material from the environment. Certain types of polymers used may form a self-healing coating or membrane, such as
40 when both an alginate and alginate producing microorganisms

are present. Surprisingly the present coating applied initially to the surface supports healing and maintenance of the initial coating by e.g. algae being present in the environment.

5 In addition to the present polymer a silicate material may be present. The silicate is considered biocompatible as well. The silicate forms a glassy structure upon contact with a polyvalent cation.

10 The silicate and/or polymer provide a conformal coating to a surface to which it is applied. The coating acts e.g. as protection against chemicals, such as salts, moisture, dust, and temperature extremes that, if uncoated (non-protected), could result in damage or failure of an underlying surface/material, and also maintains conditions of the surface, such as humidity or moisture content. The silicate provides a more stiff coating, the polymer a more flexible coating, and a combination of silicate and polymer may have in between characteristics.

15 The present composition does not or at the most to a small extent penetrate into a surface to which it is applied. 20 The membrane or coating formed can not be washed away by water, such as by rain. The membrane is fully integrated with an underlying surface, adheres thereto, and may be considered as a layer having suitable characteristics. So surprisingly the present composition may be applied directly to a surface and 25 providing advantageous effects.

It has been found that in order to have improved barrier properties further platelet nanoparticles are preferably present. Platelet nanoparticles have dimensions wherein a length, and likewise a width, thereof is significantly larger 30 than a height thereof, such as at least a factor 5 larger. A height of the nanoparticles is typically in the order of a crystallographic axis thereof, or a few times the axis, such as 1-50 nm or more. The width and length of the nanoparticles are from 10 nm - 5 μ m, preferably from 25 nm-1 μ m, more preferably from 50 nm-500 nm, such as from 100 nm-250 nm. 35

The nanoparticles are typically suspended in the aqueous composition. Once a gel and/or glassy structure is formed it has been found that the nanoparticles are incorporated therein.

40 It is an important characteristics of the present

composition that once applied onto a surface, the surface providing Fe cations (in particular Fe^{2+} and Fe^{3+}), a membrane is formed immediately, i.e. within a short time frame. As such properties of a surface are not changed significantly, e.g. by penetration of the composition or components thereof into the surface. The composition is applied at ambient temperature. On earth such a temperature relates to $-50\text{ }^{\circ}\text{C}$ - $70\text{ }^{\circ}\text{C}$, but typically modest temperatures are applicable, such as $10\text{ }^{\circ}\text{C}$ - $30\text{ }^{\circ}\text{C}$.

Once applied to a surface the present composition provides its beneficial effects thereto, without deterioration of the surface or optional underlying material. Therewith disadvantages of the prior art are overcome. A good and durable protection is provided which sticks to the surface to which it is applied well, at least under (semi-)dry conditions. For some coatings, specifically ones having alginate in it, it is found extremely difficult to remove the coating on a steel like surface if the coating is unwanted, as it sticks extremely well.

Thereby the present invention provides a solution to one or more of the above mentioned problems.

Advantages of the present description are detailed throughout the description.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates in a first aspect to a method according to claim 1.

In an example of the present method in the composition an amount (wt.%) of polymer and/or silicate is larger than an amount of nanoparticle. Ratios between amount of (ii) polymer and optional silicate (iia) (indicated as Q) and (iii)(b) amount of nanoparticle that provide advantageous characteristics to a membrane or coating formed, e.g. in terms of (im)permeability towards water, have been found to be in a range of $(Q):(iii)(b)=2:1$ to $(Q):(iii)(b)=1000:1$ (that is in almost equal amounts to an abundant polymer/silicate). It is preferred to use an amount of $(Q):(iii)(b)=5:1$ to $(Q):(iii)(b)=100:1$, such as $(Q):(iii)(b)=10:1$ to $(Q):(iii)(b)=50:1$. The ratio may vary somewhat on type of polymer/silicate used at the one hand, and on type of nanoparticles used on the other hand. It has been found that the densi-

ty of the membrane/coating formed is better under the above conditions.

In an example of the present composition the polymer and/or silicate (Q) is/are present in an amount of 1- 50 wt.%, based on a total weight of the composition. The amount of polymer/silicate may be adjusted to e.g. ambient conditions, such as temperature, humidity, and to a surface to which the present composition may be applied, etc. If a flexible coating or membrane is required, an amount of polymer is higher, whereas if a stiff coating is required an amount of silicate may be higher. Depending on a type of polymer/silicate an amount may be higher, e.g. if a gel is somewhat difficult to form at low amounts thereof. If it is preferred to have a relative permeable coating a somewhat lower amount is preferred. The amount is preferably 2-30 wt.%, more preferably 5- 20 wt.%, such as 10-15 wt.%. In general, these amounts provide the best characteristics.

In an example of the present composition the polymer is one or more of an anionic polysaccharide, such as alginate, poly vinyl alcohol, poly (meth)acryl amide, acidic polymer, poly styrene sulphonate, poly (meth)acrylic acid, acidic biopolymers, pectin, carrageenan, gelatin, a synthetic acid polymer, wherein the polymer may comprise one or more of a phosphate, sulphate and carboxylic group, and proteins. Polysaccharides may be defined as having a general formula of $C_x(H_2O)_y$ wherein x is a large number between e.g. 50 and 10000. Considering that the repeating units in the polymer backbone are often six-carbon monosaccharides, the general formula can also be represented as $(C_6H_{10}O_5)_n$ wherein as an example $10 \leq n \leq 3000$. In other words relatively small to relatively large molecules are considered. As such the present invention is in principle applicable with a relative wide range of anionic bio-degradable polymers. The type of polymer may be selected and adapted to specific requirements and boundary conditions. Some polymers relate to products obtainable from waste, such as sludge, for instance waste alginate. From an economical point of view these latter may be preferred.

In an example of the present method iron is provided as a polyvalent cation. To some extent, in as far as present in an iron or steel surface, other polyvalent cations

may support formation of the present membrane, such as one or more of calcium, copper, strontium, cobalt, zinc, magnesium, manganese, molybdenum, nickel, chromium, titanium, vanadium and niobium, preferably non-toxic cations, such as calcium, and magnesium, preferably calcium. The present invention can as a consequence in this respect be applied widely.

In an example of the present composition (iii)(b) the nanoparticles are one or more of a natural or artificial clay, the clay preferably a monovalent cation clay. The clay preferably has a cationic exchange capacity of 2-200 meq/100 grams clay at a pH of 7, more preferably 5-150 meq/100 grams, even more preferably 10-120 meq/100 grams. It has been found that clays having a relatively higher CEC perform better in terms of relevant characteristics for the present invention. The clay may comprise one or more of H^+ , Na^+ , K^+ , Li^+ . The clay may be a tetrahedral-octahedral-tetrahedral (TOT)-clay (or 2:1 clay), such as a kaolin clay, such as kaolinite, dickite, halloysite and nacrite, a smectite clay, such as bentonite, montmorillonite, nontronite and saponite, an illite clay, a chlorite clay. Also a silicate mineral, such as mica, such as biotite, lepidolite, muscovite, phlogopite, zinnwaldite, clintonite, and allophane, are applicable as well as platelet like particles. A clay applied may further be selected in view of required characteristics of a final coating. Addition of nanoparticles may improve present characteristics, e.g. (decreased) permeability towards water, structural integrity, strength, flexibility, etc.

In an example of the present composition the nanoparticles are present in an amount of 0.01- 12 wt.%, preferably 0.1- 10 wt.%, more preferably 0.5- 5 wt.%, based on a total weight of the composition. It is noted that relatively low amounts of nanoparticles may be used, which low amounts may still provide improved characteristics of the present invention. Higher amounts may be preferred, e.g. in view of (decreased) permeability, stiffness, integrity, etc.

In an example of the present composition may comprise further additives, such as an anti-fouling additive. An example thereof is $CuSO_4$. Additives may be added directly to the composition, if compatible, or may be added after applying the composition. Further additives, such as UV-

blocker, stabilizers, fillers, colorants, and pigments may be added. The amount of additives is typically < 5 wt.%, preferably smaller than 2 wt.%, such as < 1 wt.%.

5 The present invention relates to a method of forming a bio-compatible membrane making use of the present composition. Therein the present composition may be used as such, and similarly a first composition comprising the present polymer/silicate and a second composition comprising the present nanoparticles, if present, may be used. The two compositions
10 may be applied separately to a surface, and then mixing of the compositions may take place. As mixing may be less optimal in view of present characteristic of a coating being formed, application of one composition is typically preferred. The present surface, e.g. iron and steel, provides polyvalent cations, such as Fe^{2+} . It has been found that a good coating is
15 obtained by applying the present composition. Surprisingly a (semi) solid surface like that of steel is capable of providing polyvalent cations in sufficient amounts to form a membrane/coating according to the invention, and wherein the composition does not (or slightly at the most) penetrate the surface. Even further, without further measures the present method is capable of forming a membrane with required characteristics.

25 The present method may be repeated, e.g. if a thicker coating is required, if characteristics of the subsequent coating may or should vary, etc.

In an example of the present method the surface is pre-treated and/or pre-shaped. Such may improve adhesion of the present membrane or coating. The present coating applied
30 to the surface inherently has a same (or at least similar) shape.

In the present method the surface is one or more of steel, stainless steel, iron, iron alloy, cast steel, and combinations thereof. These types of materials are widely used
35 and formed and the present coating/membrane may provide advantageous characteristics to these materials.

In an example of the present method the polymer is Na-alginate, preferably a non-food grade alginate, such as obtained from a waste material handling system, such as a
40 sludge. The alginate may be obtained from bacteria, especially

from granules. The alginate from sludge is very cheap, provides better characteristics than alginate from algae, can not be used in food or the like, and is therefore considered a very good material for the present invention.

5 In an example of the present method the clay is Na-montmorillonite.

In an example of the present method the composition is applied in an amount of 10-1000 ml/m², such as 10-500 ml/m². Surprisingly a relatively thin coating is sufficient to
10 provide the present advantages. A coating of 1-10 µm thickness is typically sufficient.

In a second aspect the present invention relates to a method of protecting a surface from degradation according to claim 10. As indicated throughout the application especially
15 an iron comprising surface is considered.

In an example the surface is protected from one or more of drying, oxidizing, such as corroding, wearing, fouling, and dehydrating.

In a third aspect the present invention relates to a
20 coating according to claims 11 or 12.

In an example the coating is stiff, comprising Fe cations, water, optionally platelet nanoparticles, and one or more of an in water dissolvable cyclic and single chain silicate.

25 In an example the coating is flexible. It is noted that combinations of polymers may be used, as well as combinations of nanoparticles, in order to obtain required characteristics.

In an example the present coating is applied in an
30 environment comprising algae. The algae may provide alginate for maintaining properties of the present coating. For instance, if iron or steel is applied in salty aqueous conditions, such as in a sea or ocean, a coating applied will remain effective, e.g. in terms of protection. It has been found
35 that the present membranes improve a life time of underwater iron and steel, such as in ships, in offshore, and in piping, and reduce maintenance costs thereof.

In a fourth aspect the present invention relates to one or more of steel, stainless steel, iron, iron alloy, cast
40 steel, comprising a water impermeable flexible polymer coating

according to the invention.

In an example the coating has a thickness of 5-500 μm , more preferably a thickness of 10-250 μm , such as a thickness of 50-100 μm . In view of the amounts of water and components a relatively thicker coating (e.g. 100 μm) would still require a low amount of composition (0.1 l/m^2), i.e. is practically not very limiting.

In a fifth aspect the present invention relates to a use of the present composition and/or of the present flexible polymer coating for protecting steel, stainless steel, iron, iron alloy, or cast steel, from degradation.

The invention is further detailed by the accompanying figures and examples, which are exemplary and explanatory of nature and are not limiting the scope of the invention. To the person skilled in the art it may be clear that many variants, being obvious or not, may be conceivable falling within the scope of protection, defined by the present claims.

SUMMARY OF FIGURES

Fig. 1.(a) shows a picture of a treated steel plate and fig. 1.(b) shows a picture of an untreated steel plate. Fig. 2.(a) shows a picture of a treated steel plate and fig. 2.(b) shows a picture of an untreated steel plate.

DETAILED DESCRIPTION OF FIGURES

The figures are further detailed in the description of the experiments below.

EXAMPLES/EXPERIMENTS

The invention although described in detailed explanatory context may be best understood in conjunction with the accompanying examples and figures.

In a first experiment various combinations of polymer, nanoparticle, silicate, respectively, and clay were tested. The experiment consisted of pouring solutions on a steel surface. All but one mentioned exhibited rapid gel formation when they got into contact with the steel surface, the surface providing Fe ions. The results are summarized in the table below.

Table 1:

Sample Na				
Alginate	Na MMT	Na_2SiO_3	Result	

11

	1	+	-	-	+
	2	+	+	-	+
	3	+	+	+	+
	4	+	-	+	+
5	5	-	+	-	0
	6	-	+	+	0
	7	-	-	+	0

The alginate relates to a bacterial alginate, obtained from sludge. MMT relates to montmorillonite. Therein a "+" indicates rapid formation of a gel, the gel having characteristics in line with the description above. "0" indicates forming of a gel, but questionable if the gel has all the characteristics mentioned. For example the gels of samples 5-7 cracked upon drying. "-" indicates no gel being formed.

The concentrations of Na-alginate in samples 1, 2, 3 and 4 is 2wt.%, and concentrations of NaMMT and Na₂SiO₃ is about 5 wt.% with respect to the weight of Na alginate: in total composition that relates to 2 wt.% of Na Alginate and 0.107 wt.% of Na₂SiO₃ and/or 0.107 wt.% of NaMMT. The concentration for samples 5 and 7 was 2 wt.%, for NaMMT and Na₂SiO₃, respectively. And for sample 6, the concentration was 2 wt.% of Na₂SiO₃ and about 5 wt.% of NaMMT on the weight of Na₂SiO₃; in total composition that relates to 2 wt.% of Na₂SiO₃ and 0.107 wt.% of NaMMT.

Inventors performed further tests regarding alginate on steel surface, for corrosion protection. The test consisted of two cleaned (non-corroded) steel plates, from which one was immersed in sodium alginate solution and dried afterwards. The thickness of alginate film was around 100 µm. The steel plates were immersed in 35g/L NaCl solution, and inventors monitored the corrosion visually. Inventors observed initial protection of the steel plate with an alginate film. It was clear that a corrosion product of the untreated steel plate sedimentated in the solution (orange sediment), while in the alginate treated one there was only some iron (ions) in the solution. The steel plates were taken out of the NaCl solution, and what was observed on the steel plate with alginate was a gel layer on the surface of steel plate, which is considered to be a Fe Alginate gel. After inventors removed the gel, it was observed that the steel plate was not corroded (fig. 1a), whereas the

steel plate without alginate was corroded (fig. 1b).

In a further experiment inventors have applied sodium alginate on a steel surface that has been corroding in 35g/L NaCl solution. The sodium alginate film was dried at 40 °C, and a thickness thereof was about 100 µm. A difference with the previous experiment was seen immediately, because the color of the film turned brown. Such is considered indicative for some Fe Alginate forming (fig. 2a). The steel plates were placed in 35g/L NaCl solution and what was observed was swelling of the polymer film. Conform the previous experiment precipitation of corrosion products for the non-treated steel plate was seen. It is noted that adhesion of the gel was partially successful, possibly because conditions applied were not optimal (yet). Such may be due to the film preparation. It is however obvious from the figs. 2a and 2b, respectively, that treated steel was much better protected from corrosion than non-treated steel.

In a more quantitative approach the following test was performed. A first steel plate was left to corrode in 35g/L NaCl solution, after which it was dipped in 3 wt.% NaAlginate. The coated steel plate was dried, with coating thickness of around 100 µm. The corrosion period took 4 days in 35g/L NaCl solution. Coated and uncoated steel plates were dipped in NaCl solution. Visually, in first day coated steel plate corroded less (no sedimentation of corrosion product). After 4 days it was not possible to visually judge solution of coated steel plate. Inventors removed both steel plates from the solutions and dried the solution, at 105°C for 24h, to measure the mass of the corrosion product. The measured mass loss was from evaporation of water. The corrosion-product mass was obtained by the difference between the measured dry mass and the NaCl mass, which inventors derived from the NaCl initial concentration. The mass loss was calculated as follows:

Concentration of NaCl = $m(\text{NaCl}) / (m(\text{NaCl}) + m(\text{H}_2\text{O}))$

$m(\text{dried mass}) = m(\text{NaCl}) + m(\text{Corrosion product})$

The results were the following:

$m(\text{Corrosion product}) = 0.893\text{g}$ ---> For coated steel

$m(\text{Corrosion product}) = 2.871\text{g}$ ---> Steel without coating

The submerged surfaces were determined in order to validate the results further. The surface of the uncoated

steel plate was 55cm² and for the coated it was 46.9 cm². In the case of the coated steel plate, some dried mass could also come from the coating itself, because we saw some part of the coating going into the solution (it detached); in other words
5 the 0.893 grams above relates to an upper estimate. From the above one may conclude that coating steel with an alginate membrane reduces corrosion (in salty water) with approximately a factor 3. Such is considered remarkable.

10 It should be appreciated that for commercial application it may be preferable to use one or more variations of the present system, which would similar be to the ones disclosed in the present application and are within the spirit of the invention.

CLAIMS

1. Method of forming a durable and not-ready removable bio-compatible membrane comprising the steps of

providing an aqueous composition comprising for at least 95 wt.% (based on a total weight of the composition)

5 (i) water, and optional co-solvents, the co-solvents being selected from glycerol, and alcohols, such as ethanol and methanol,

(ii) an anionic bio-degradable polymer, and/or a synthetic acid polymer, wherein the polymer is capable of
10 forming a gel in contact with polyvalent cations under ambient conditions, the polymer being dissolved in the liquid, wherein the polymer is present in an amount of 1- 50 wt.%, and optionally

(iii)(a) one or more of an in water dissolvable
15 cyclic and single chain silicate (SiO_{2+n}^{2n-}), such as silicate (SiO_3^{2-}), and orthosilicate (SiO_4^{4-}), pyrosilicate ($\text{Si}_2\text{O}_7^{6-}$), such as a monovalent cations thereof, and components that form a silicate such as SiO_3^{2-} in water, wherein the silicate is capable of forming a glassy structure in contact with polyvalent
20 cations under ambient conditions, wherein the silicate is present in an amount of 1- 50 wt.%, based on a total weight of the composition, and

(iii)(b) platelet nanoparticles, the nanoparticles being suspended in the liquid either as such or in parts
25 thereof, wherein the nanoparticles are present in an amount of 0.01- 12 wt.%,

applying the composition onto a surface at ambient temperature (-50 °C- 70 °C), the surface providing Fe cations, wherein the surface is one or more of steel, stainless steel,
30 iron, iron alloy, cast steel, and combinations thereof,

reacting the (ii) bio-degradable polymer and/or (iii)(a) silicate, and Fe cations, thereby forming a membrane layer on the surface.

2. Method according to claim 1, wherein the pH of the
35 composition is 6-12.

3. Method according to any of the preceding claims wherein, in the composition an amount (wt.%) of polymer and/or silicate is larger than an amount of nanoparticle.

4. Method according to any of the preceding claims, wherein the polymer is one or more of an anionic polysaccharide, such as alginate, poly vinyl alcohol, poly (meth)acryl amide, acidic polymer, poly styrene sulphonate, poly

5 (meth)acrylic acid, acidic biopolymers, pectin, carrageenan, gelatine, a synthetic acid polymer, wherein the polymer may comprise one or more of a phosphate, sulphate and carboxylic group, and proteins, and/or

wherein further polyvalent cations are provided,
10 such as one or more of calcium, copper, strontium, cobalt, zinc, magnesium, manganese, molybdenum, nickel, chromium, titanium, vanadium and niobium, preferably non-toxic cations, such as calcium, and magnesium, preferably calcium.

5. Method according to any of the preceding claims,
15 wherein

(iii)(b) the nanoparticles are one or more of a natural or artificial clay, the clay preferably a monovalent cation clay, comprising one or more of H^+ , Na^+ , K^+ , Li^+ , such as a TOT-clay (or 2:1 clay), such as a kaolin clay, such as kaolinite, dickite, halloysite and nacrite, a smectite clay, such as bentonite, montmorillonite, nontronite and saponite, an illite clay, a chlorite clay, a silicate mineral, such as mica, such as biotite, lepidolite, muscovite, phlogopite, zinnwaldite, clintonite, and allophane, and platelet like polymers, and
20 wherein the nanoparticles are present in an amount of 0.1- 10 wt.%, based on a total weight of the composition.

6. Method according to any of the preceding claims, wherein the surface is pre-treated and/or pre-shaped.

7. Method according to any of the preceding claims,
30 wherein the composition consists for more than 98 wt.% of water and optional co-solvents, an anionic bio-degradable polymer, and/or a synthetic acid polymer, and optionally a silicate and nanoparticles, and less than 2 wt.% additives.

8. Method according to any of the preceding claims,
35 wherein the polymer is Na-alginate, and wherein the clay is Na-montmorillonite, and/or wherein the composition is applied in an amount of 1-1000 ml/m^2 .

9. Method according to any of the preceding claims,
40 wherein the composition is applied at least once by one or

more of spraying, brushing, nebulizing, and pouring.

10. Method of protecting a surface from degradation by performing a method according to any of the preceding claims.

5 11. Stiff coating comprising Fe cations, water, optionally platelet nanoparticles, and one or more of an in water dissolvable cyclic and single chain silicate, obtainable by a method according to any of claims 1-10.

10 12. Flexible coating comprising Fe cations, water, optionally platelet nanoparticles, and bio-degradable polymers, obtainable by a method according to any of claims 1-10.

 13. Self-healing flexible polymer coating according to claim 12, wherein the coating is applied in an environment comprising algae.

15 14. One or more of steel, stainless steel, iron, iron alloy, cast steel, comprising a water impermeable flexible polymer coating according to claim 12 or 13, preferably a coating having a thickness of 5-500 μm , more preferably a thickness of 10-250 μm , such as a thickness of 50-100 μm .

20 15. Use of a flexible polymer coating according to claim 12 for protecting steel, stainless steel, iron, iron alloy, or cast steel, from degradation.

